Advances in Residue Hydrocracking using the LC-FINING platform

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Outline

- Factors Impacting High Conversion of Residue
  - Nature of Vacuum Residue
  - Reliable Reactor Systems
  - Economic Viability – What is the optimum conversion level?
- CLG LC-FINING Technology Platform
  - Extensive Commercial Experience
- Extending LC-FINING Platform to Higher Conversion
  - LC-MAX and LC-SLURRY

CLG Offers All Heavy Oil Conversion Technologies

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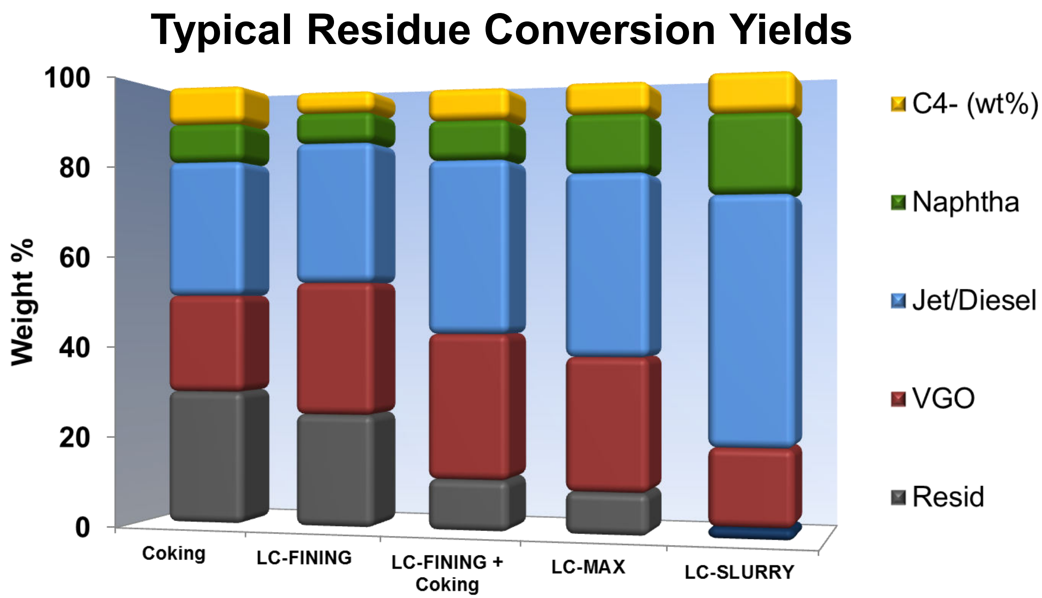
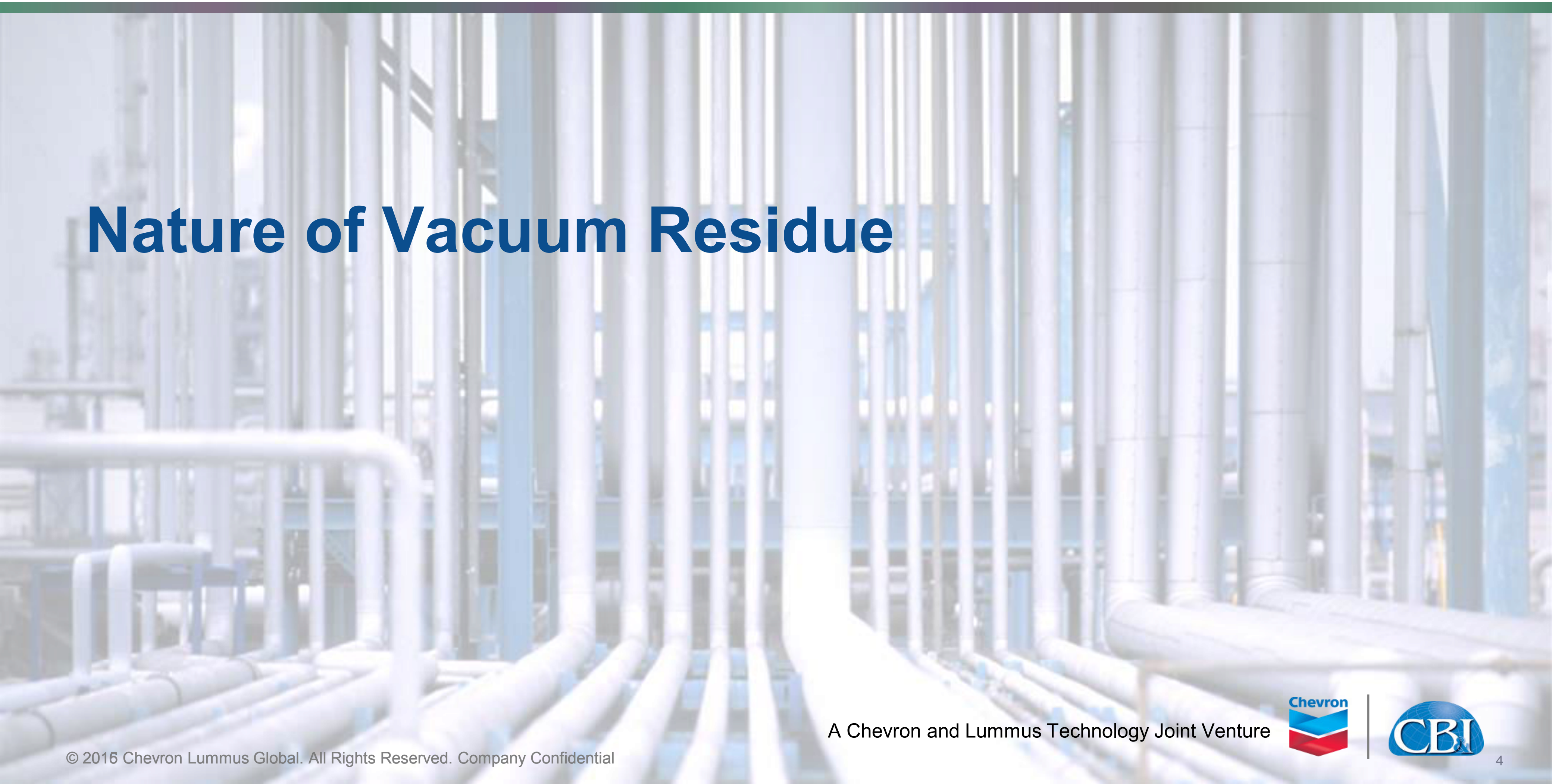
- Residue Hydrocracking:
  - LC-FINING and LC-MAX
  - Chevron LC-SLURRY*
- Residue Hydrotreating:
  - VRDS, ARDS, OCR, UFR
- CB&I SDA and Coking*
- Have complimentary hydroprocessing technologies:
  - ISOCRACKING
  - ISOTREATING



CLG is uniquely positioned to support any residue upgrading project

*Added in January 2015

Nature of Vacuum Residue



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Distribution of CCR in AH Crude

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Short-Path Distillation Cuts of Arabian Heavy Vacuum Resid

Property	Lightest Cut	Middle Cut	Heaviest Cut	Weighted Average	Feed
Cut Range, GCSD, °F	975-1120	1120-1305	1305+		975+
Yield, Wt % Resid	25.4	20.0	54.6	100	100
Carbon, Wt %	84.48	84.15	83.20	83.72	83.67
Hydrogen, Wt %	11.24	10.95	9.19	10.06	10.18
Sulfur, Wt %	3.99	4.28	6.23	5.27	5.13
Oxygen, Wt %	0.35	0.34	0.61	0.49	0.54
Nitrogen, Wt %	0.22	0.25	0.58	0.42	0.42
Total	**100.28**	**99.97**	**99.81**	**99.96**	**99.94**
H/C Atomic	1.59	1.55	1.32	1.43	1.45
Nickel, ppm	2	13	98	57	55
Vanadium, ppm	18	80	285	176	190
Conrad. Carbon, Wt %	5.0	11.6	36.9	23.7	22.1

Courtesy: Irvin A. Wiehe

Composition of the Heaviest Fractions of Crude

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Elemental Analysis of Preparative HPLC Fractions of Arabian Heavy 1305°F+

Fraction	Yield, Wt %	C, Wt %	H, Wt %	H/C (Atomic)	S, Wt %	N, Wt %	Σ Elements, Wt %
Saturates	1.8	85.78	13.59	1.89	0.46	NA	99.83
1-Ring Aromatics	1.5	84.96	12.54	1.76	2.08	NA	99.58
2-Ring Aromatics	4.3	84.04	11.97	1.70	2.86	NA	98.87
3-Ring Aromatics	4.9	83.52	11.07	1.58	4.79	NA	99.38
4-Ring Aromatics	14.2	82.10	10.12	1.47	6.30	NA	98.52
Polars 1	12.2	82.41	8.83	1.28	6.88	0.87	98.99
Polars 2	1.6	81.26	8.45	1.24	6.72	0.54	96.97
Polars 3	2.9	81.77	8.58	1.25	6.42	0.81	92.87
Asphaltenes	56.6	82.18	8.15	1.18	8.07	0.92	99.32
Total	**100.0**	**82.42**	**9.00**	**1.30**	**5.95**	**0.66**	**98.94**
1305°F+ Total	100.0	83.20	9.19	1.32	6.23	0.58	99.20

Courtesy: Irvin A. Wiehe

CCR to Diesel – Hydrogen Consumption

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- CCR has ~ 3.8 wt % hydrogen
- Euro V Diesel requires ~14.5 wt % hydrogen to meet S.G. specifications
- In order to convert 25 wt % CCR in VR to Diesel, we will require 10.7 wt % hydrogen! This will not be viable under many scenarios.
- Smart CCR conversion is key to residue hydrocracking

What Are These Asphaltenes That Cause Us So Much Grief?

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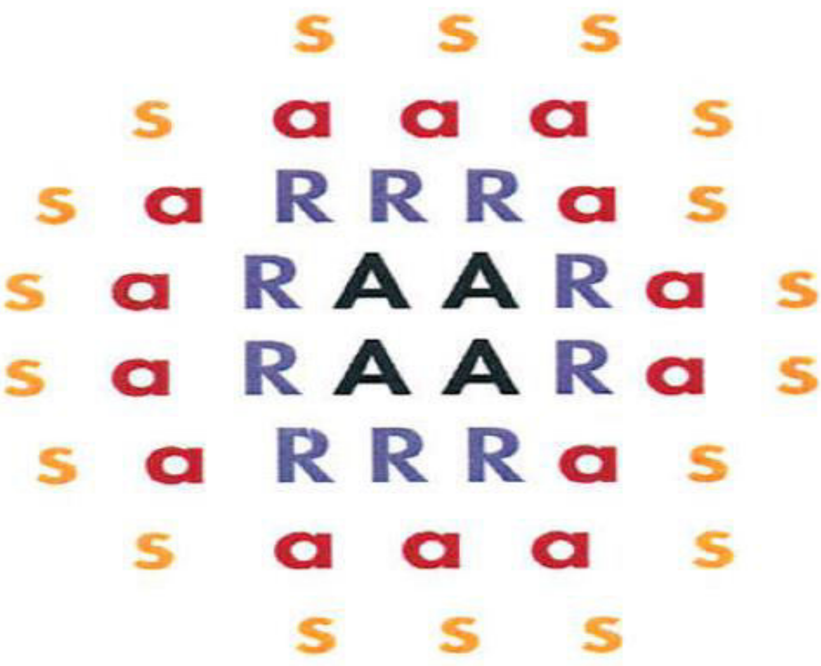
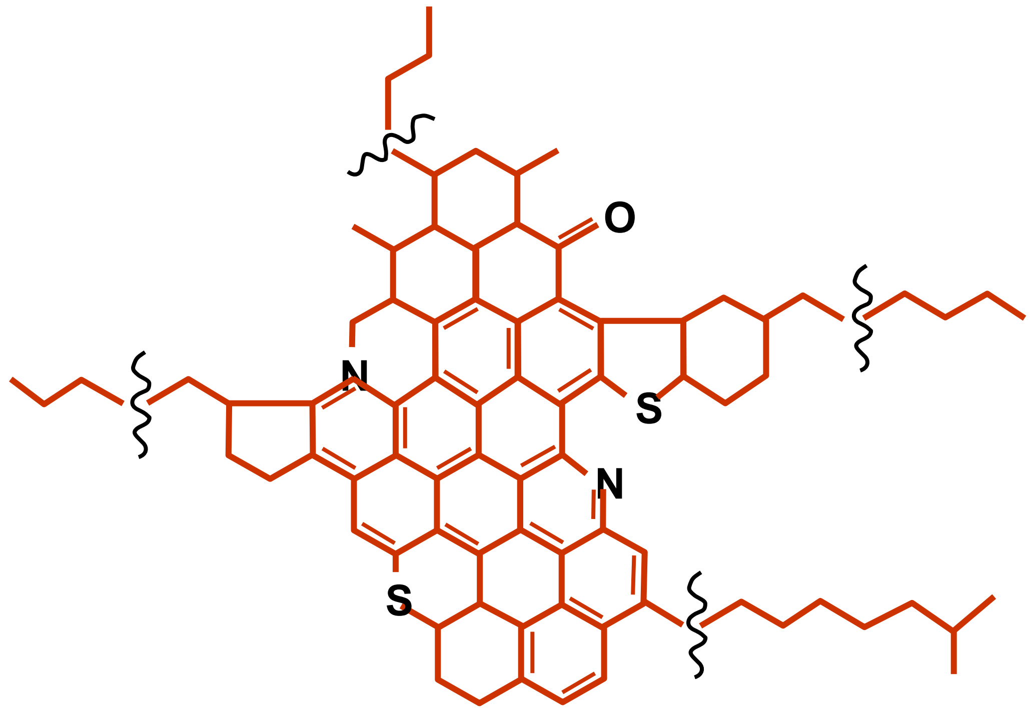


s – saturates
a – aromatics
R – Resins
A – Asphaltenes



Asphaltenes are very high MW polar compounds suspended in resins. Thermal or hydrocracking disturbs this natural order!

What We Know Thus Far…

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- Asphaltenes can be of many different types – with varying degree of processing challenges
- CLG has developed proprietary methods (5-solvent and others) to identify the bad and ugly ones
- Once identified, we can, to a large extent, predict at what conversion level the converted, heaviest asphaltenic cores will drop out of solution
- This knowledge defines the maximum conversion that is possible without serious reactor downstream equipment fouling

Sediments limit max. conversion.
CLG has large database of commercial data.

How Far Can We Push Conversion?

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- Pure Thermal (CCR of Product > CCR of Feed)
- Ebullated Bed (mass transfer – disadvantage of conventional catalyst pores) – 65-82%
- Transition Metal Sulfides (small dispersed catalysts overcome the mass transfer disadvantages) – promise to achieve >95% conversion but nanoparticles do not remain nano! LC-SLURRY catalyst was developed recognizing this limitation and designed to overcome it.
- But is it worth it?
  - Very high hydroconversion requires hydrogenating and cracking outside ring of PNA's
  - Process is very slow because hydrogen donation from partially hydrocracked PNA reacts much faster to form C_1-C_4 gases than cracking of saturated ring
  - Final product of deepest conversion is 4- and 5- ring HPNA and C_1-C_4 gases. The 4- and 5- ring HPNA have very high S.G. and are extremely difficult to convert to diesel.
  - Increasing from 90 to 95% conversion can double reactor size in both residue and subsequent distillate hydrocracking.

Need for Reliability in Residue Hydrocracking

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- High contaminant levels: asphaltenes, CCR, metals
- Operating severity favors thermal cracking and potential for coke deposit
- Requires very careful attention to equipment design, piping, valving, addition of diluents…
- Attention to safety and emergency procedures
- Commercial experience is key to Best Practices – cannot be simulated in pilot plants

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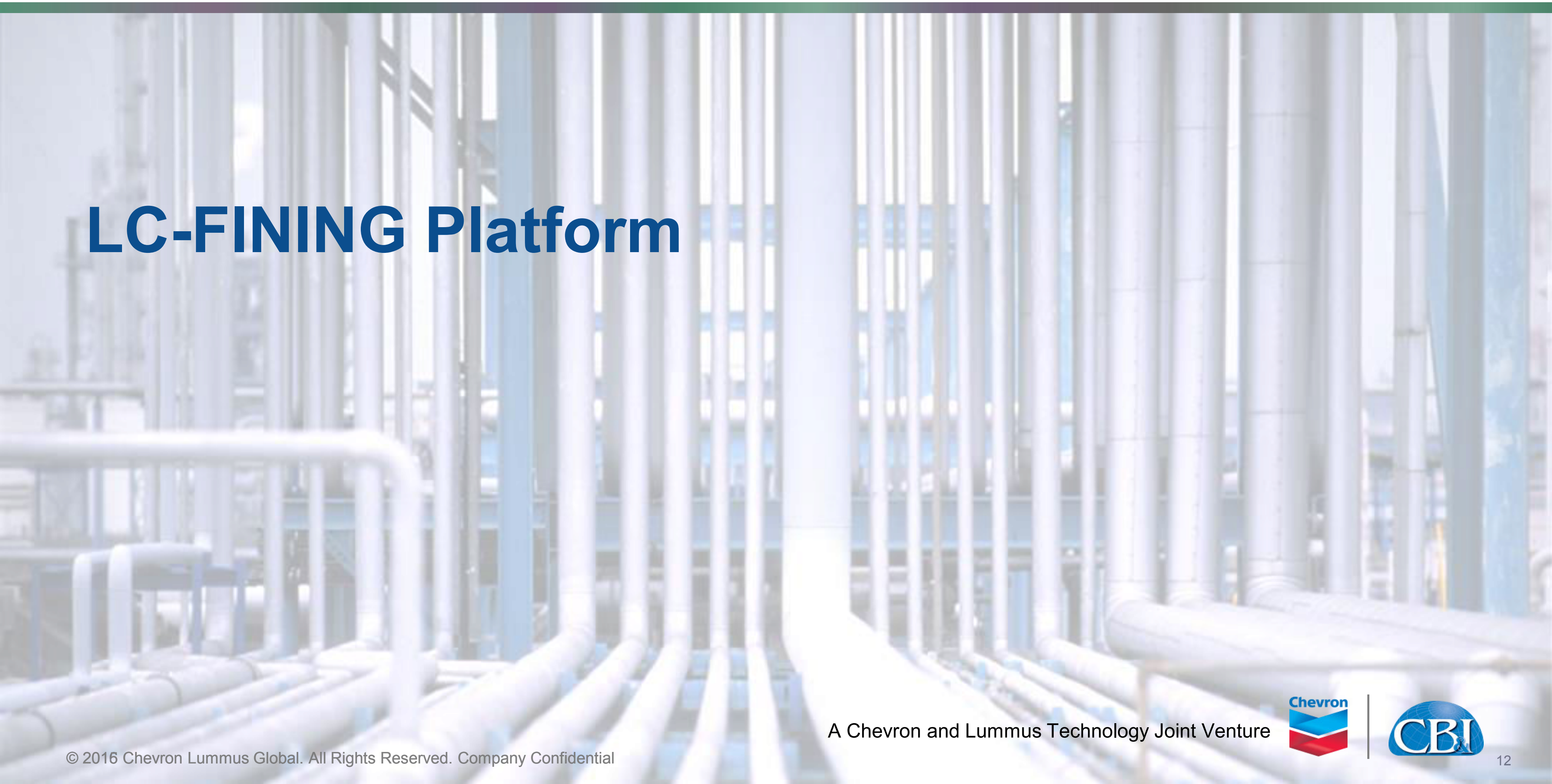
LC-FINING Platform



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Robust LC-FINING Ebullated Bed Residue Hydrocracking Technology Platform

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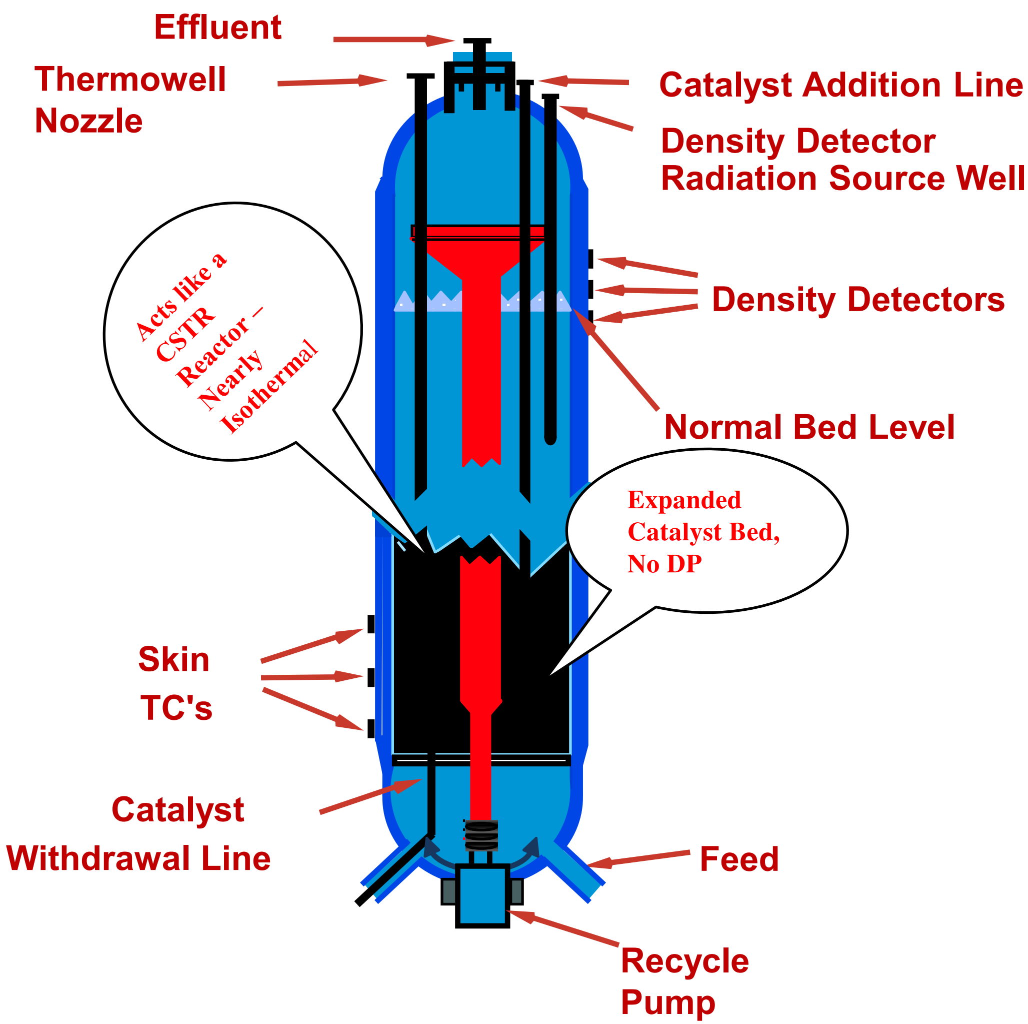
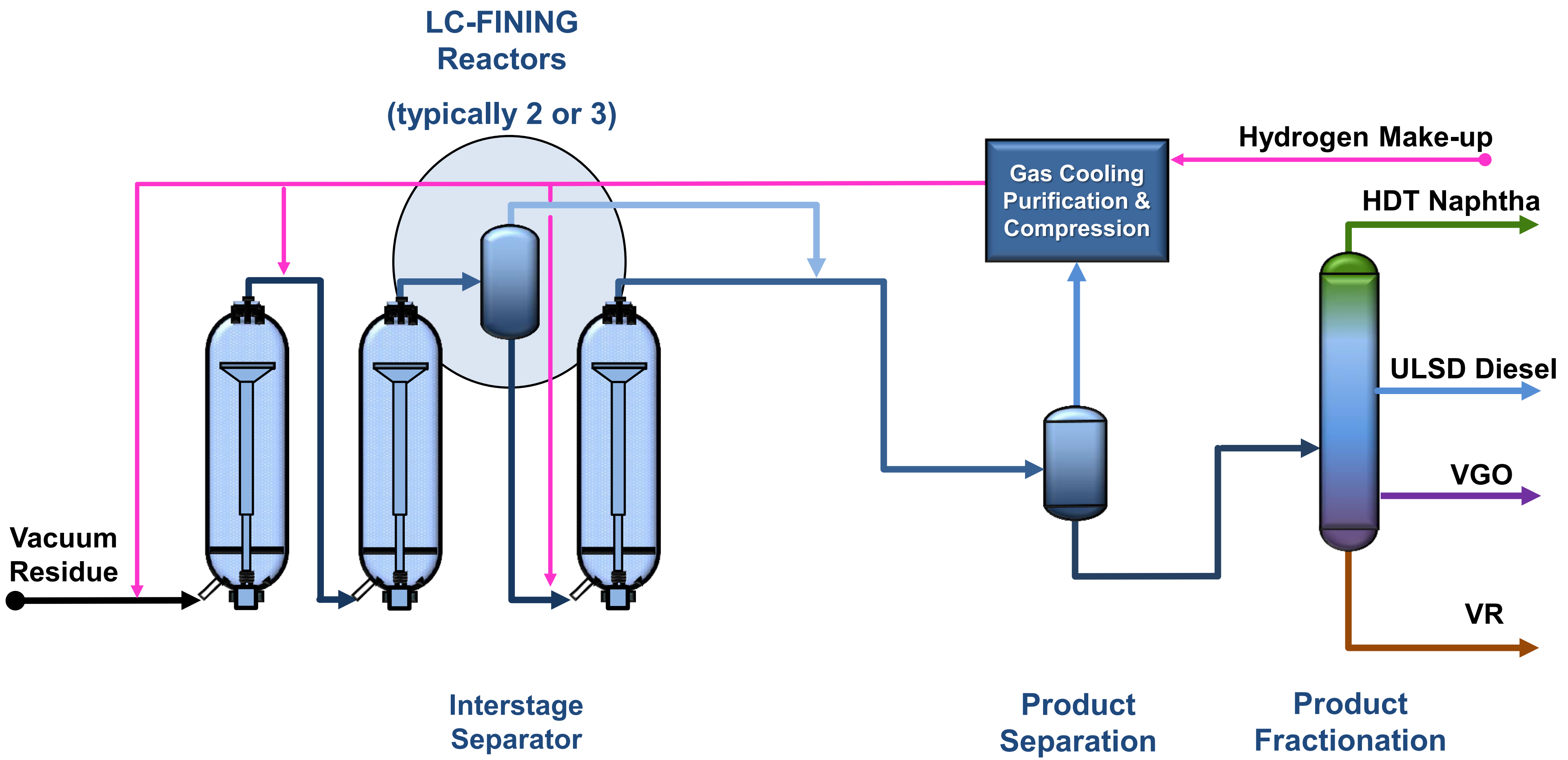


Reactor Temperature	410–440°C (770-824°F)
Reactor Pressure	110–180 bar (1600-2600 psig)
Resid Conversion	55–80%
Hydrogen P.P.	75–125 bar (1100-1800 psi)
Chem H_2 Consumption	135–300 Nm^3/m^3 (800-1780 scfb)
Desulfurization	60–85%
CCR Reduction	40–70%
Demetallization	65–88%

LC-FINING with Interstage Separator Increases Conversion and Capacity



- Reduces vapor superficial velocity and gas hold-up
- Extends per train capacities 65 to 75 percent
- Up to 75,000 BPD per reactor train

LC-FINING with Integrated Hydrotreating Produces Clean High Quality Products

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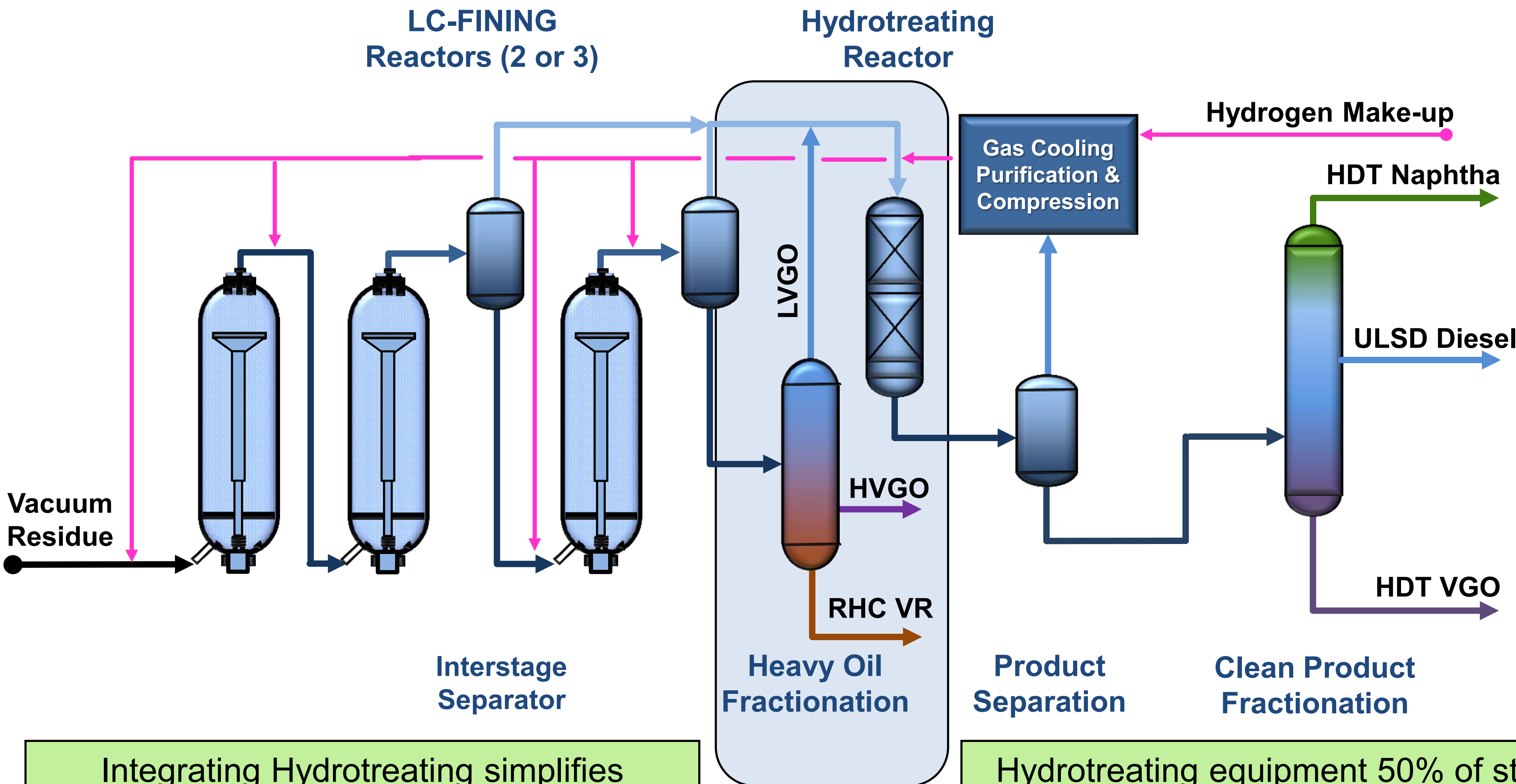

Integrating Hydrotreating simplifies fractionation and produces clean products

Hydrotreating equipment 50% of stand alone unit, 60-70% of standalone cost

CLG Residue Hydrocracking Products Upgrading Background is Absolutely Essential

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- CLG is the only licensor with commercial experience of **hydrocracking** residue hydrocracking-derived VGO to Euro V Diesel quality (Neste Oy, Finland).
- Most other refiners process residue hydrocracking-derived VGO in FCC units via FCC feed pretreaters.
- CLG has also hydrocracked RDS-derived VGO in KNPC for decades and in ENI Taranto for over 5 years.
- Hydroprocessing and especially deep HDN and hydrocracking of VGO derived from residue hydrocracking requires special catalyst systems and operating conditions to prevent rapid catalyst deactivation.
- CLG-designed units can now operate trouble-free for 3 to 5 years.

Residue Hydrocracked VGO From Urals

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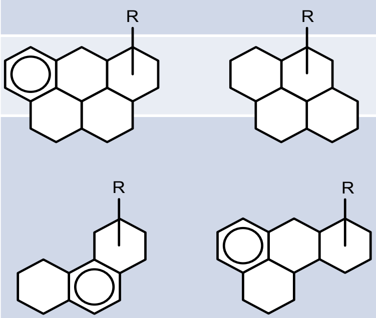
Mid-Boiling Point, °C	Polycyclic Index (PCI), ppm
385	1,800 **(AL VGO <1,500; AH VGO <3,800)**
440	7,000
455	10,000 **(Coker Gas Oil From Lagoven-7,000 wppm; Whole DAO = 10,000)**
482	17,000
500	20,000



- Need to control Residue Hydrocracked VGO End Point to even lower levels than SR VGO to avoid processing high aromatic components

LC-FINING with Integrated Two-Stage Hydrocracking Maximizes High Value Distillates

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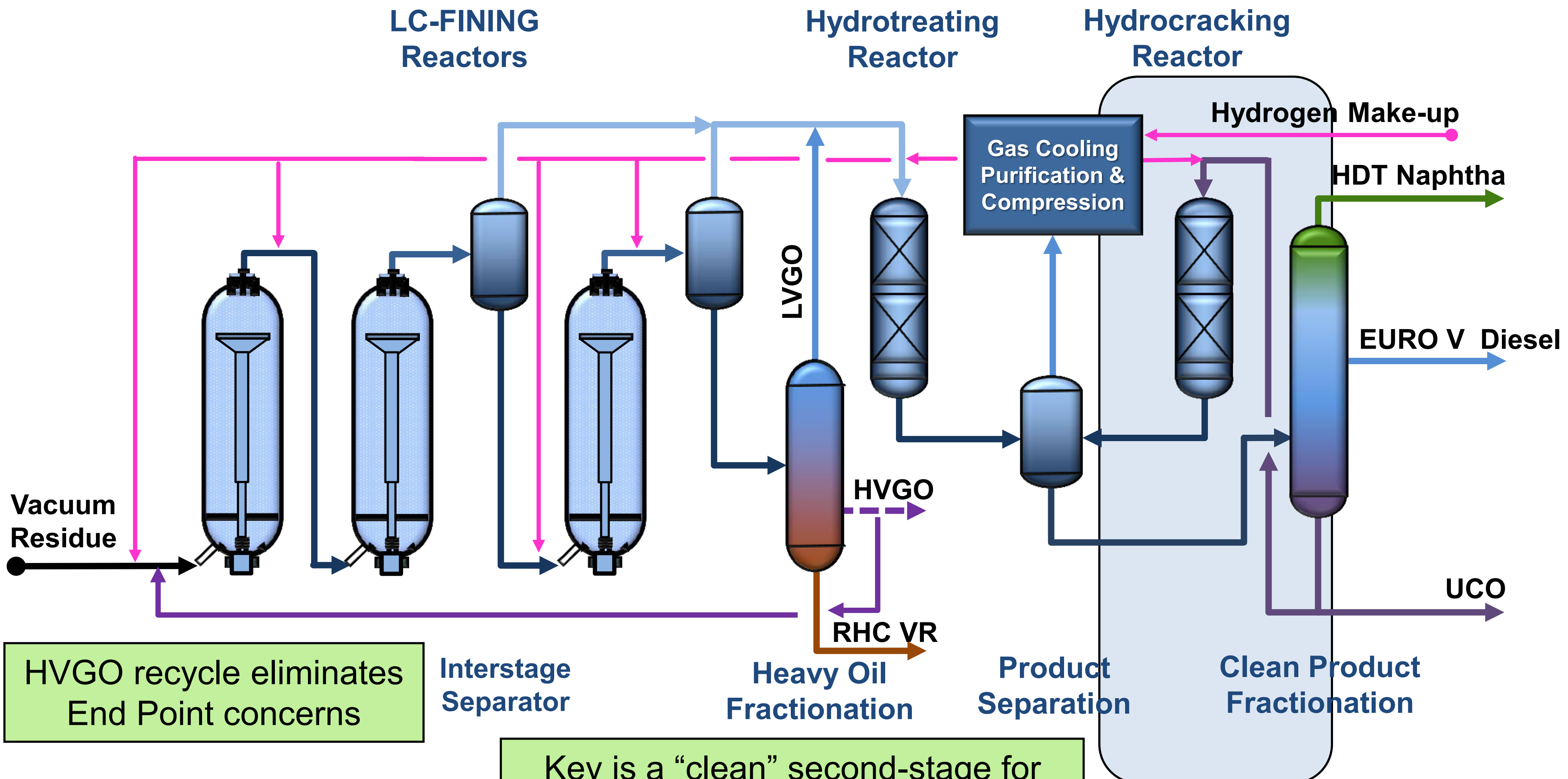

HVGO recycle eliminates End Point concerns

Key is a "clean" second-stage for Selective Cracking to Euro V Diesel

Neste Porvoo, LC-FINING With Integrated ISOCRACKING Facility to Make Euro V Diesel

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CLG LC-FINING / LC-MAX Commercial Experience

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Startup	Client	BPSD	MTPA	Processing Objective
2020	Confidential, Western Europe**	38,000	2.05	Stable LSFO
2020	Confidential, South East Asia*	72,000	4.07	LC-MAX @ 90% Conversion
2019	BAPCO, Bahrain	68,000	3.75	Coker Feed
2018	Russia	1,000	0.6	Coker Feed
2017	Sincier, China	50,000	2.76	LC-MAX @ 90% Conversion
2017	Northwest Upgrading, Canada	30,000	1.66	Synthetic Crude Oil
2010	GS Caltex, S. Korea	66,000	3.64	Stable Fuel Oil
2010	Shell Canada / AOSP, Canada	47,300	2.61	Synthetic Crude Oil
2007	Neste Oil, Finland	40,000	2.21	Stable Fuel Oil
2003	Shell Canada / AOSP, Canada	46,000	2.54	Stable HO
2003	Shell Canada / AOSP, Canada	46,000	2.54	Stable HO
2000	Slovnaft, Slovakia	25,000	1.38	Stable LSFO
1998	Eni/RAM, Italy	25,000	1.38	Stable LSFO
1988	Syncrude Canada	50,000	2.76	Coker Feed
1984	Marathon (Formerly BP), USA	75,000	4.14	Coker Feed
	Total	**641,300**	**36.0**	

- ***August 2015 award. Includes integrated large VGO Hydrocracker. Competitively bid and won against other Residue Hydrocracker licensors (one ebullated bed and two slurry hydrocracking licensors)**
- ****** September 2015 award**

LC-MAX

Increases Conversion to 90%

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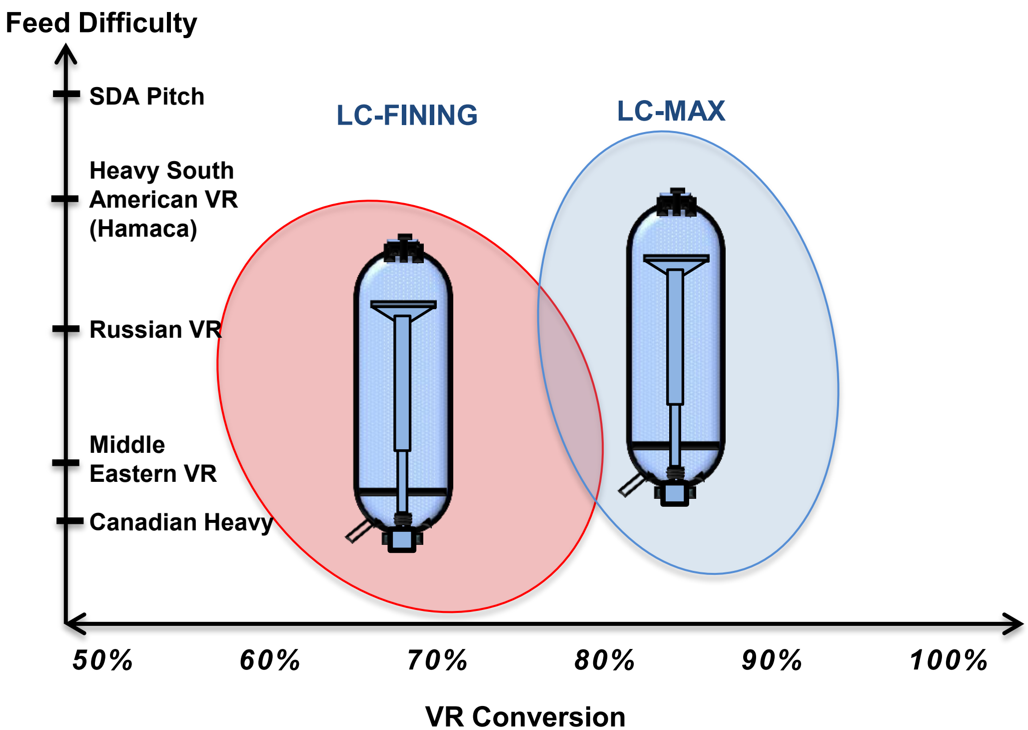
LC-MAX
Expands Range of LC-FINING Applications

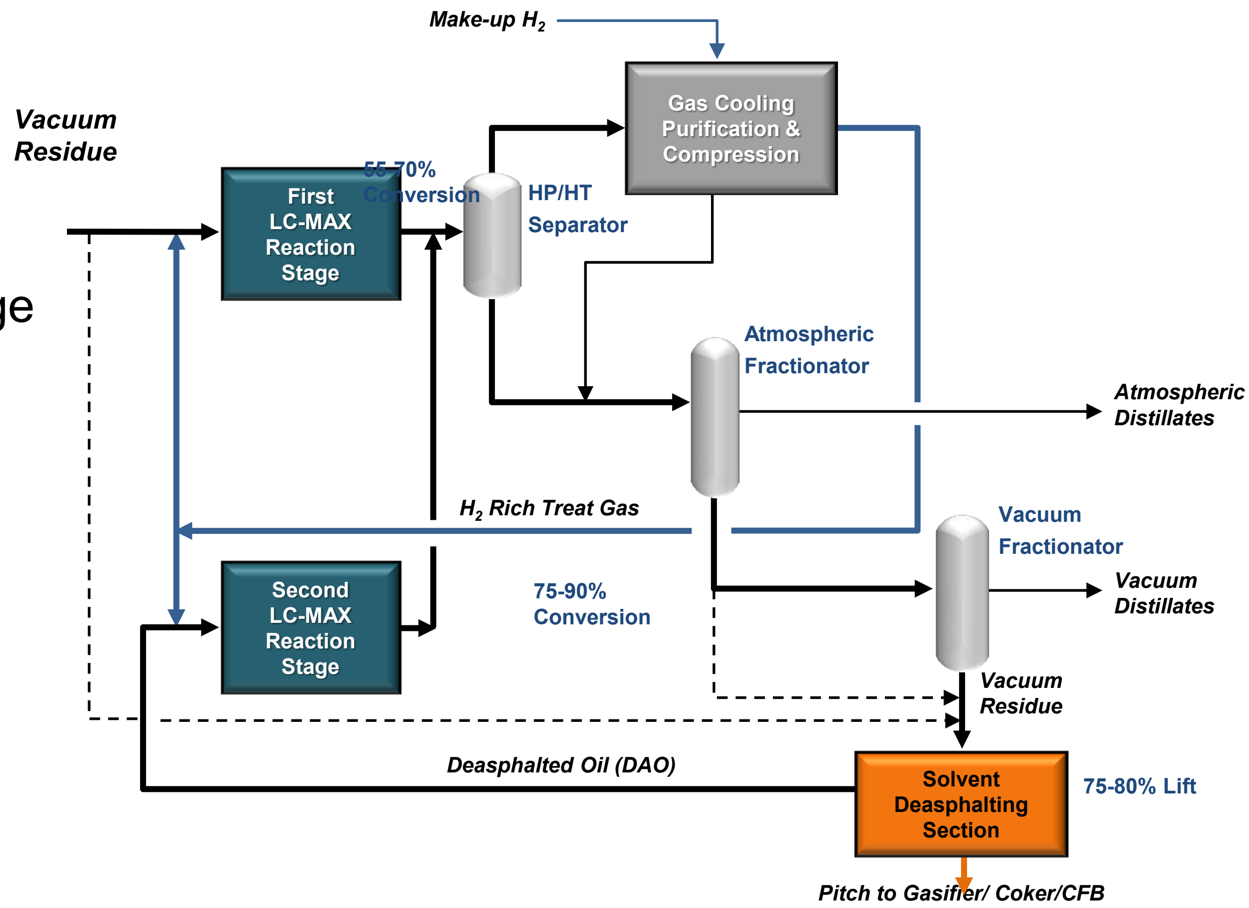


LC-MAX

- Obtains high conversion (85-90%) in a single process
- Based on the combination of proven LC-FINING and SDA technologies.
- An excellent solution for refiners who want high conversion and can utilize the unconverted residue such as for power and steam generation
- Has better selectivity at the same conversion level than thermal slurry hydrocracking processes

LC-MAX

- LC-FINING with Integrated SDA
- First stage severity relaxed below any possibility of sediment formation
- High lift SDA rejects first stage unconverted Asphaltenes
- DAO sent to second stage
- Second stage reactor has higher severity as minimal sediment formation
- Feed flexibility
- SDA Pitch ~ 8-10%



Comparison of Economic Factors with very difficult Urals Feed

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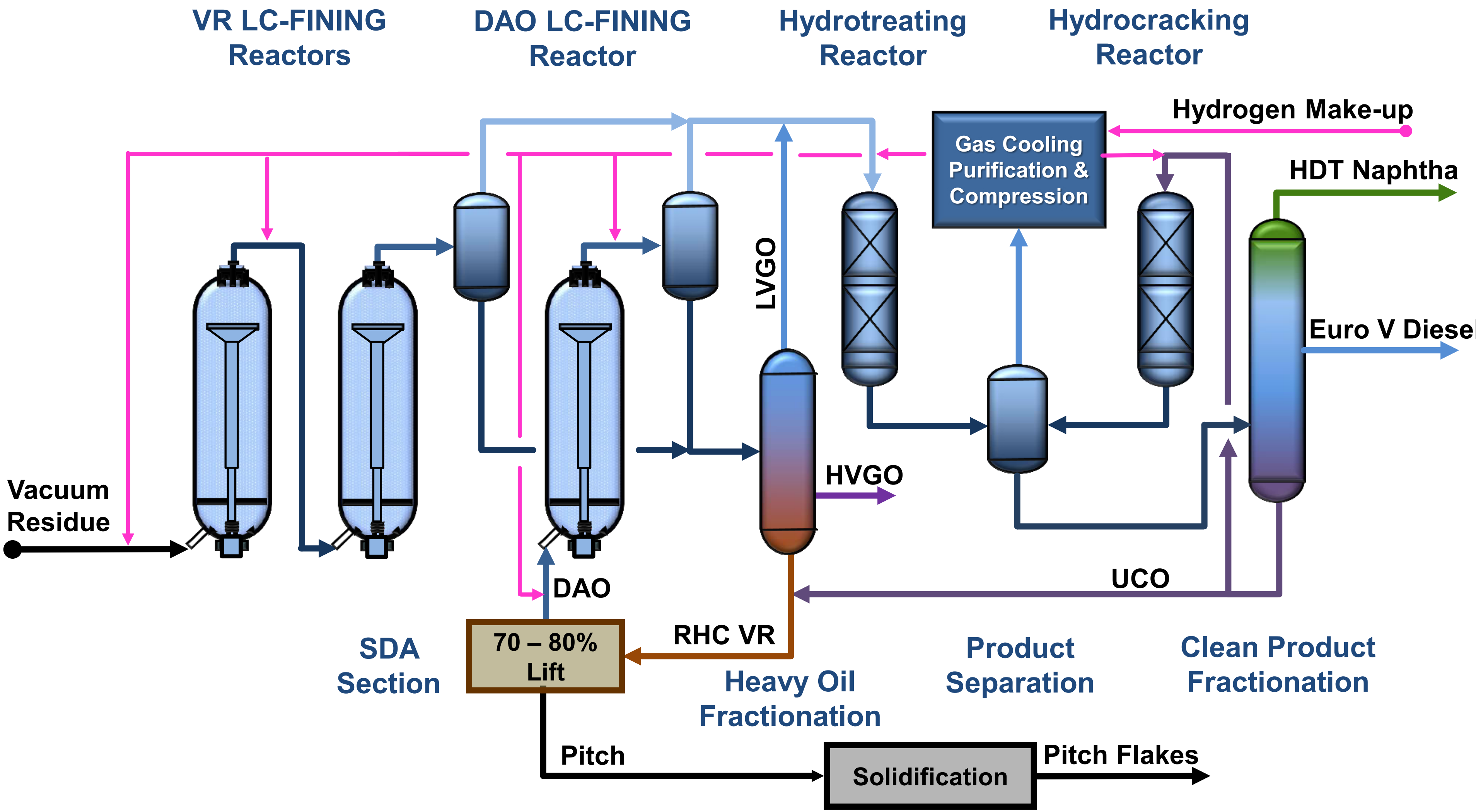
Comparison of Economic Factors LC-MAX vs Standalone LC-FINING				
	Standalone LC-FINING	**LC-MAX**		
		1st Stage	**2nd Stage**	**Overall**
Capacity, tph	100	100	36	98
Residue Conversion, wt%	65	60	77	90+
Reactor Volume Ratio	Base	0.65 Base	0.33 Base	0.9 Base
Catalyst Addition Rate	Base	0.75 Base	0.13 Base	0.88 Base
Chemical H2 Cons. Ratio	Base	0.75 Base	0.4 Base	1.15

- With most feeds, conversion of 90%+ can be achieved while maintaining low sediment levels in the UCO and minimal fractionator back end fouling
- Verified in large scale pilot plants on:
  - Urals (Russian Export) VR
  - Middle East Heavy VR

LC-MAX with Integrated Hydrocracking



Unconverted Residue Solutions

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- LC-MAX:
  - Case 1 Pitch properties:
    - S.G. : 1.23
    - Sulfur: 2.99 wt%
    - CCR: 59.4
    - Softening Point >175°C
  - Pitch can be burned in liquid or solid form (flakes or powder)
  - Pitch sent to E-Gas unit for gasification (Sincier Project)
  - CLG has a cost effective solidification option using Sandvick double belt flaking.
  - A CFB vendor has already certified suitability of LC-MAX Pitch
    - Have done analysis of samples from 2015 pilot plant runs after Sandvick Flaking demo run
  - Cement Manufactures have tested LC-MAX Pitch and indicated it is suitable fuel

LC- MAX Summary

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- LC-MAX is a patented and proven residue hydrocracking process based on reducing risks from already reliable LC-FINING technology platform
- Key Features of LC-MAX are 90% conversion with minimum technological risk, minimum hydrogen and minimum capital; VGO has lowest HPNA content.
- LC-MAX utilizes all the integrated hydroprocessing knowledge from Shell Canada and Neste Oil and 30+ years of LC-FINING platform in general.
- First 2.8 MM MTA LC-MAX unit will start up in 2017
- Largest single train residue hydrocracker (4.1 MM MTA) with integrated hydrocracker utilizing LC-MAX currently in engineering.

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LC-SLURRY

Increases Conversion to 97%

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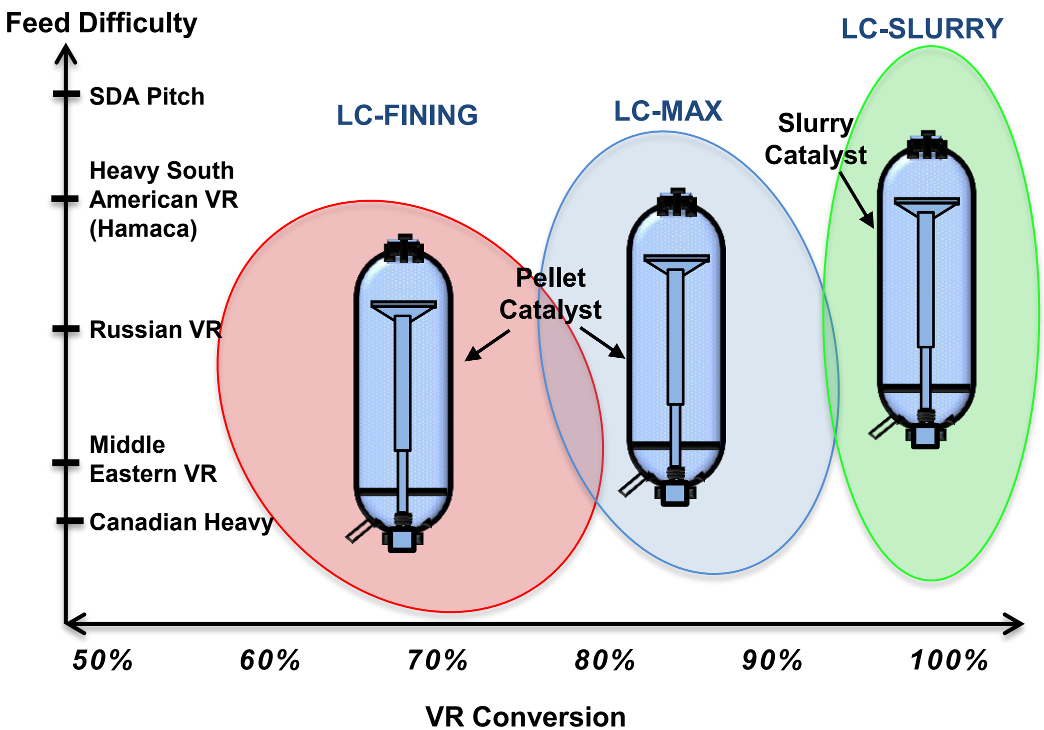
LC-SLURRY
Increased Conversion With Difficult Feeds



- Near 100% conversion of heavy oils / SDA tar to high-value products
  - 115% liquid yield
  - Over 80 vol % Euro V diesel (after VGO HC)
- Unique high activity catalyst
  - Recovered in the process
  - Eliminates fouling concerns associated with other catalyst or additive systems
- Based on LC-FINING platform
  - Commercially proven and reliable
  - Optimal reactor configuration

LC-SLURRY – Completes the CLG Residue Upgrading Portfolio

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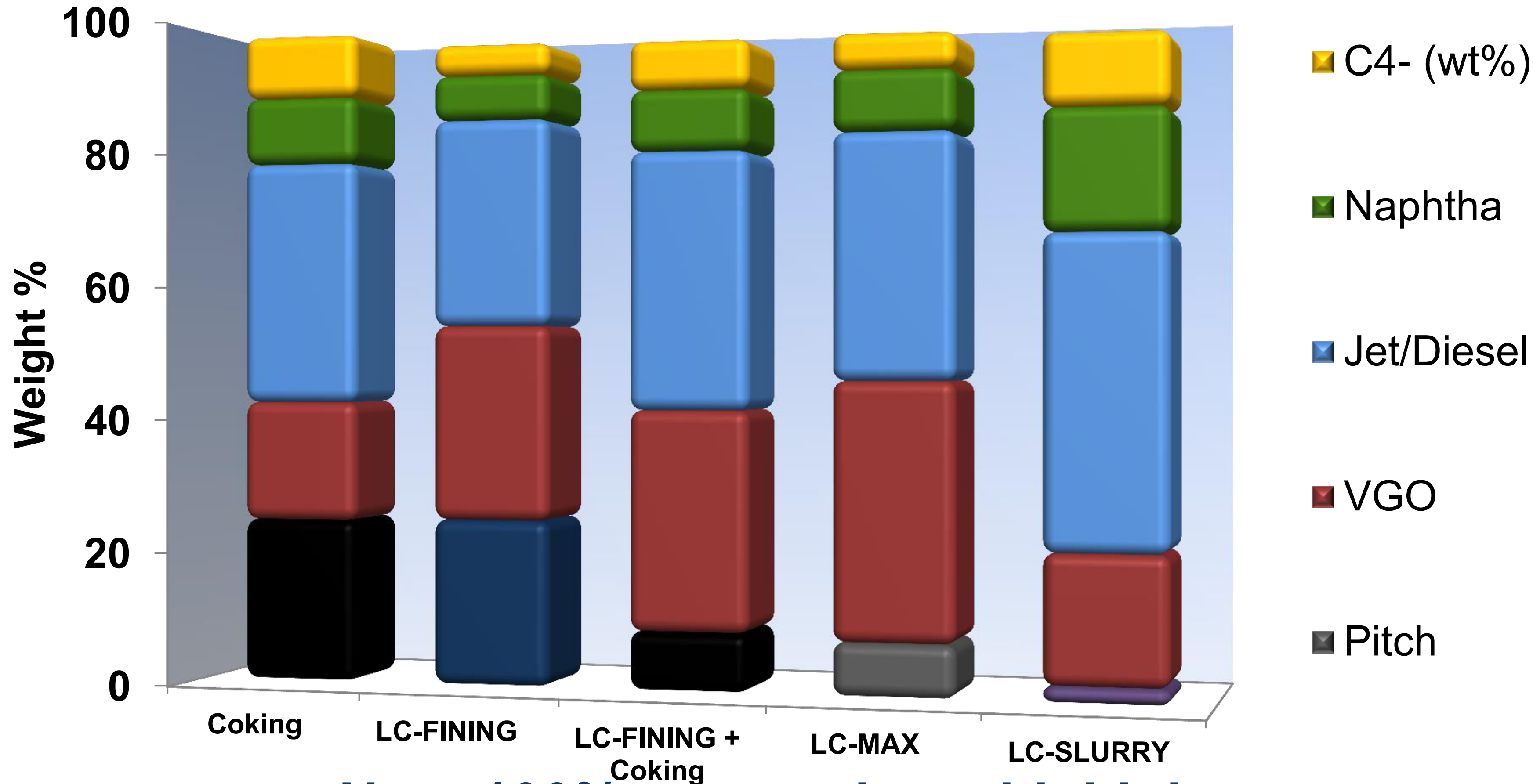

Near 100% conversion with high selectivity to liquid products

ISOSLURRY™ Catalyst
Designed for Superior Performance

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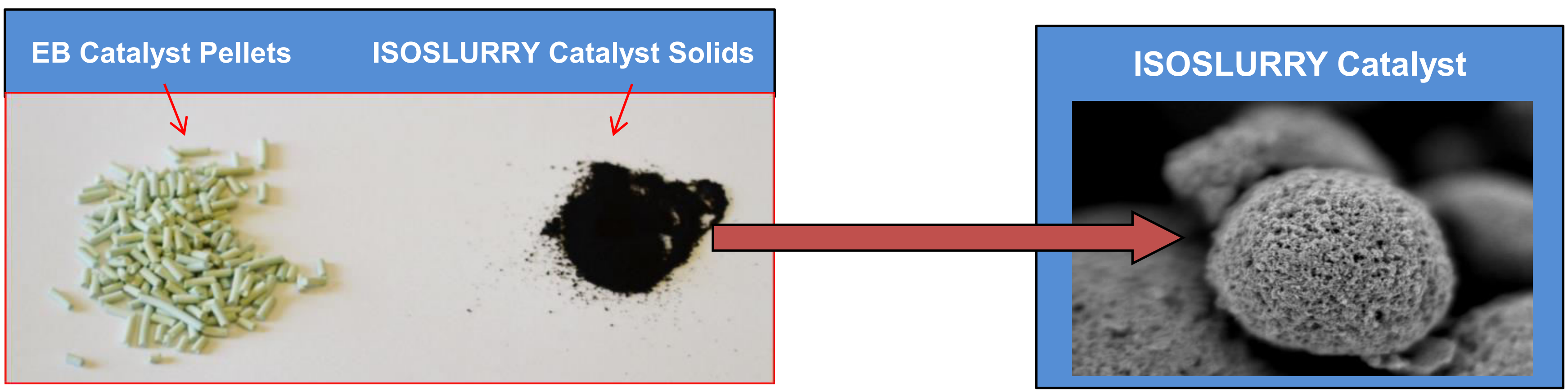
- Based on residue hydroprocessing catalyst know-how
- Unique and optimized properties
- Highly active nickel moly-based catalyst
- Excellent access to reactive sites
- Produced ex-situ to ensure high quality
- Catalyst quality and dosage
  - Keeps the system clean
  - Suppresses coke formation
  - Improves bottom oil quality
  - Allows very high conversion with reliable operation



LC-SLURRY
Upgrades the Most Difficult Molecules

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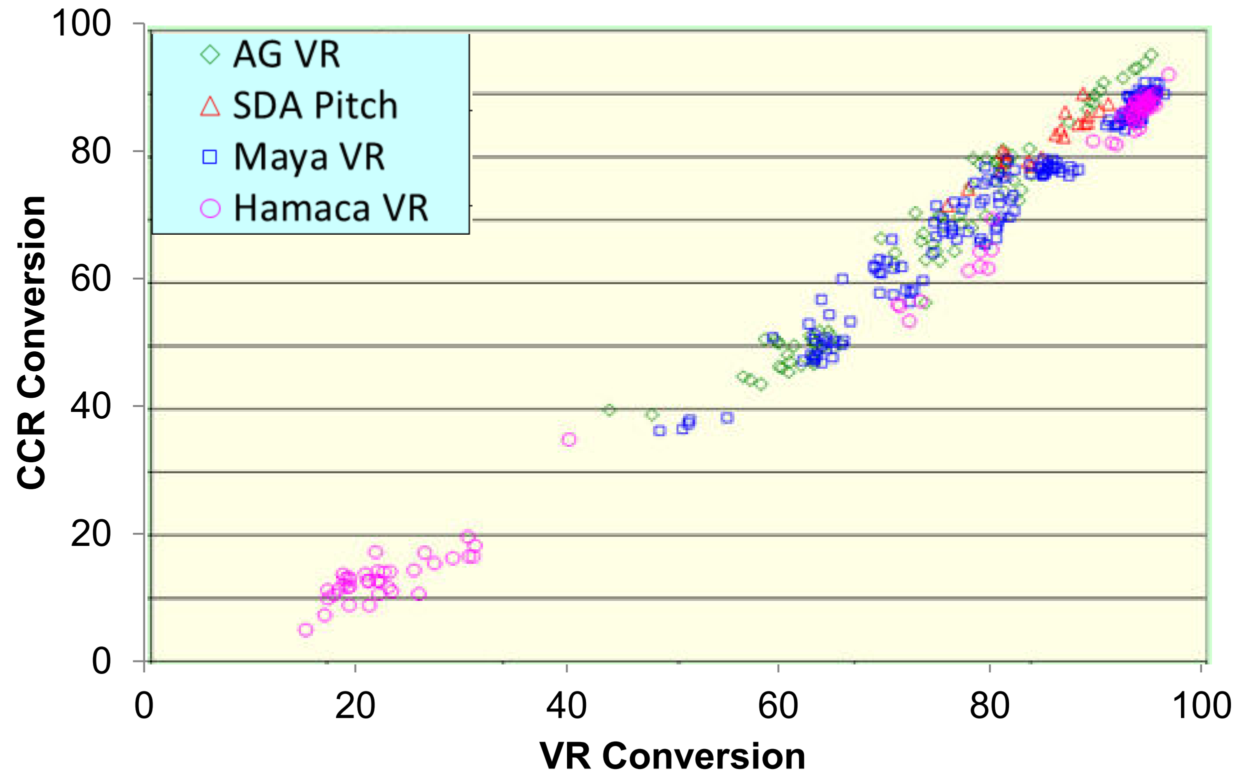
- MCR/CCR conversion tracks VR conversion
  - Avoids instability issues
  - Avoids large coke make
  - 94% HDMCR and 97% VR conversion on SDA tar
- Catalyst quality and dosage
  - Keeps the system clean
  - Suppresses coke formation
  - Improves bottom oil quality
  - Allows very high conversion with reliable operation



LC-SLURRY
Optimal Flow Scheme for Slurry Hydrocracking

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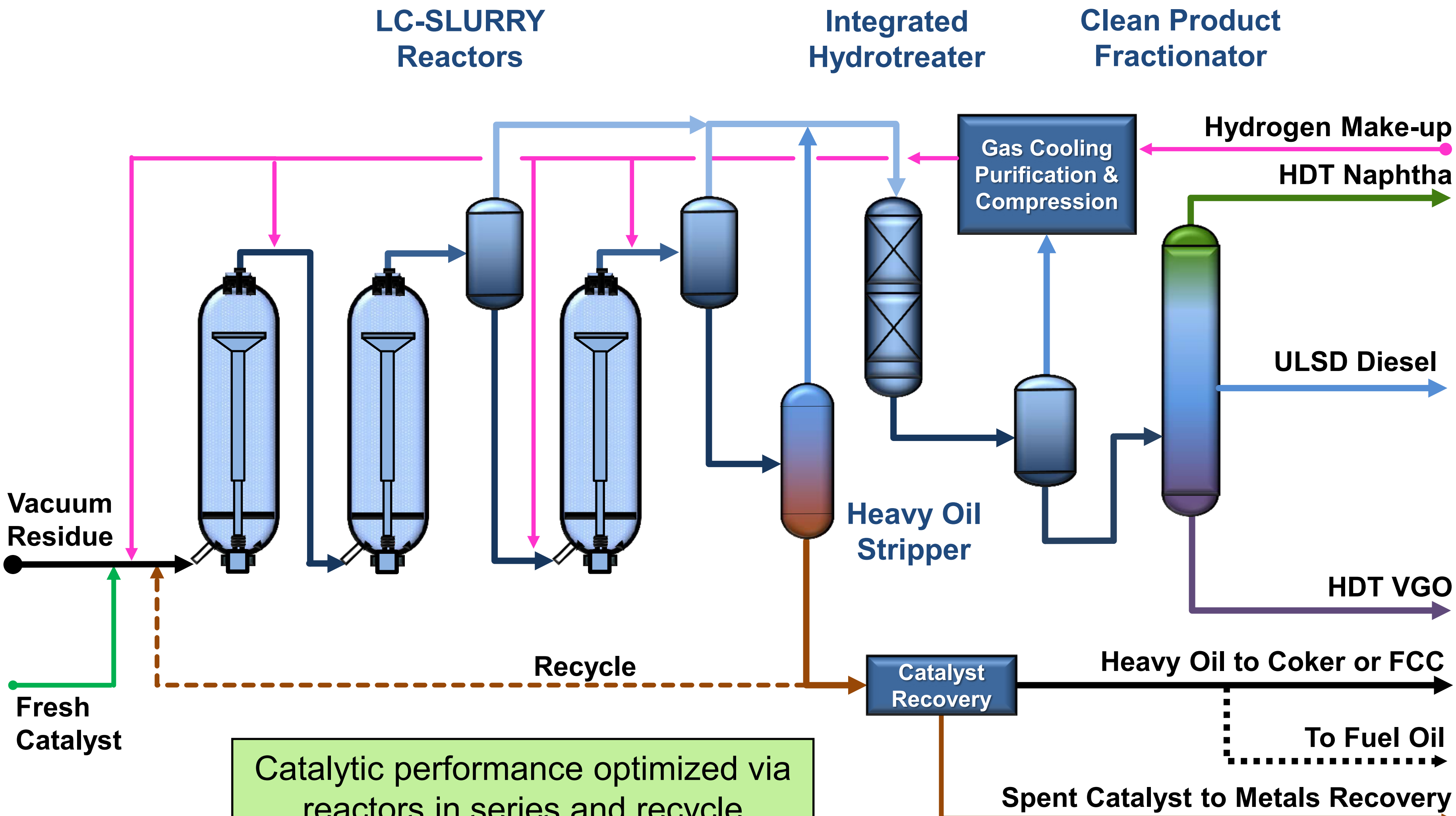

Catalytic performance optimized via reactors in series and recycle

Focus on Commercial Scale

- Demands of Full Commercial Scale as Starting Point
  - Focus on Real Equipment Performance and Reliability
  - Avoids Common Overfocus on Interesting Catalyst an Chemistry
  - Widen Test Plan to Include Critical Equipment Understanding
- Learnings from Commercial Scale Approach
  - Critical Equipment Often Absent from Pilot and Demo Scale
  - Economy of Scale Clearly Identifies Key Performance Issues
  - Challenges in Similar Commercial Units is Very Valuable
- Commercialize Only Essential New Equipment Types
  - Utilize Existing Expertise and Equipment
  - Devote Significant Resources to New Equipment or New Use

Commercial Readiness Basis

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- LC-Slurry is Adaptation of LC-FINING
  - Feeds, Conditions, Reactor Platform are Same
  - Chemistry is Superior to LC-FINING in Robustness
  - LC-FINING Unit Reliability is Good Starting Point
- Switch to Slurry Catalyst from Extrudate Catalyst
  - Reactor Operation is Actually Simpler
    - Unique LC-Slurry Catalyst Forms Non-settling Slurry
    - Continuous catalyst addition to feed
  - Much Higher Catalytic Activity Creates “Clean System”
- New Equipment is Catalyst Recovery Section
  - Robust, Redundant Design to Ensure Availability
  - Test Work in Small Commercial Scale Equipment
- Process Design same as with LC-FINING and LC-MAX
  - Changes only due to different products yields and separation requirements

LC- SLURRY Summary

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- LC-SLURRY is a step out slurry hydrocracking technology that is capable of near 100 wt% conversions selectively to high value products.
- ISOSLURRY catalyst is a generation ahead catalyst compared to any other slurry catalyst or additive. It allows full access to active sites and keeps the entire system “clean”
- It is fully ready for commercial applications as it uses the proven LC-FINING platform and has fully demonstrated the reaction section with extended high conversion runs and commercial scale catalyst recovery equipment

Design & Operation vs Reference Units

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- Equipment Design from LC-FINING
  - Stay Within Known Good Performance Range
  - Clear Best Design Practices from Commercial Units
  - Low Level Slurry Experience at 1st Oil Sands LC-FINING Unit
  - Clear Evidence that LC-Slurry is Non-Abrasive, Non-Settling
- Operation in Reference LC-FINING Units
  - History of Solving Operating/Reliability Issues
  - Information on Range of Good Operation
  - RU87 Comparison of LC-Slurry to LC-FINING
- Solving LC-FINING Challenges is Basis for LC-SLURRY
  - Ensure Change to Slurry Improves or Sustains Good Operation

LC-SLURRY Research Unit (RU-87)

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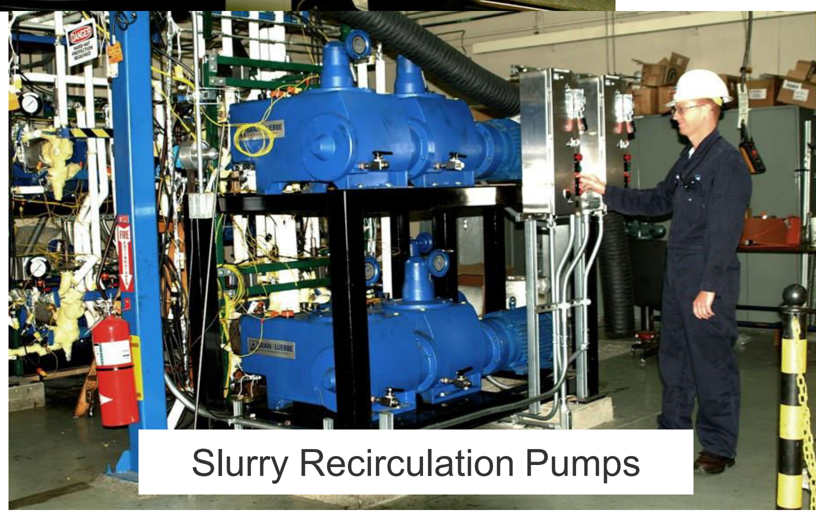
Control Station

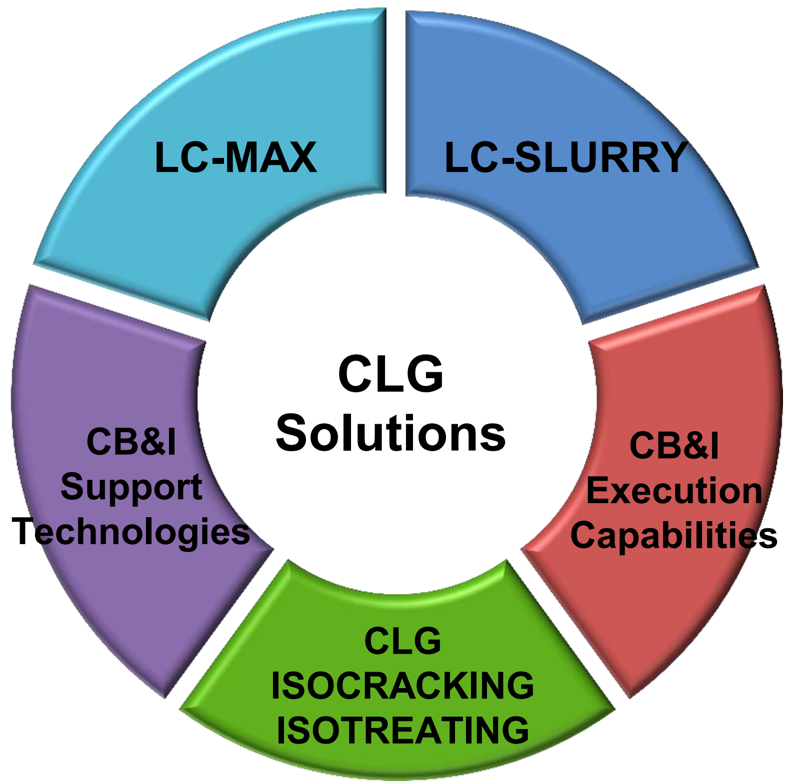


Slurry Recirculation Pumps

Liquid Recirculation Slurry Reactor (One of Three)

CLG is your One-Stop Source For Your Residue Upgrading Project

- LC-FINING is the leading proven residue hydrocracking technology
- Have high conversion solutions based on LC-FINING
  - **LC-MAX** - 90% conversion, commercially proven sections
  - **LC-SLURRY** 97% conversion, LC-FINING platform and advanced slurry catalyst
- Have leading Hydroprocessing technologies
  - ISOTREATING
  - ISOCRACKING
- Have CB&I support technologies
  - Hydrogen
  - Sulfur recovery
- Have Fast Track Project Solutions



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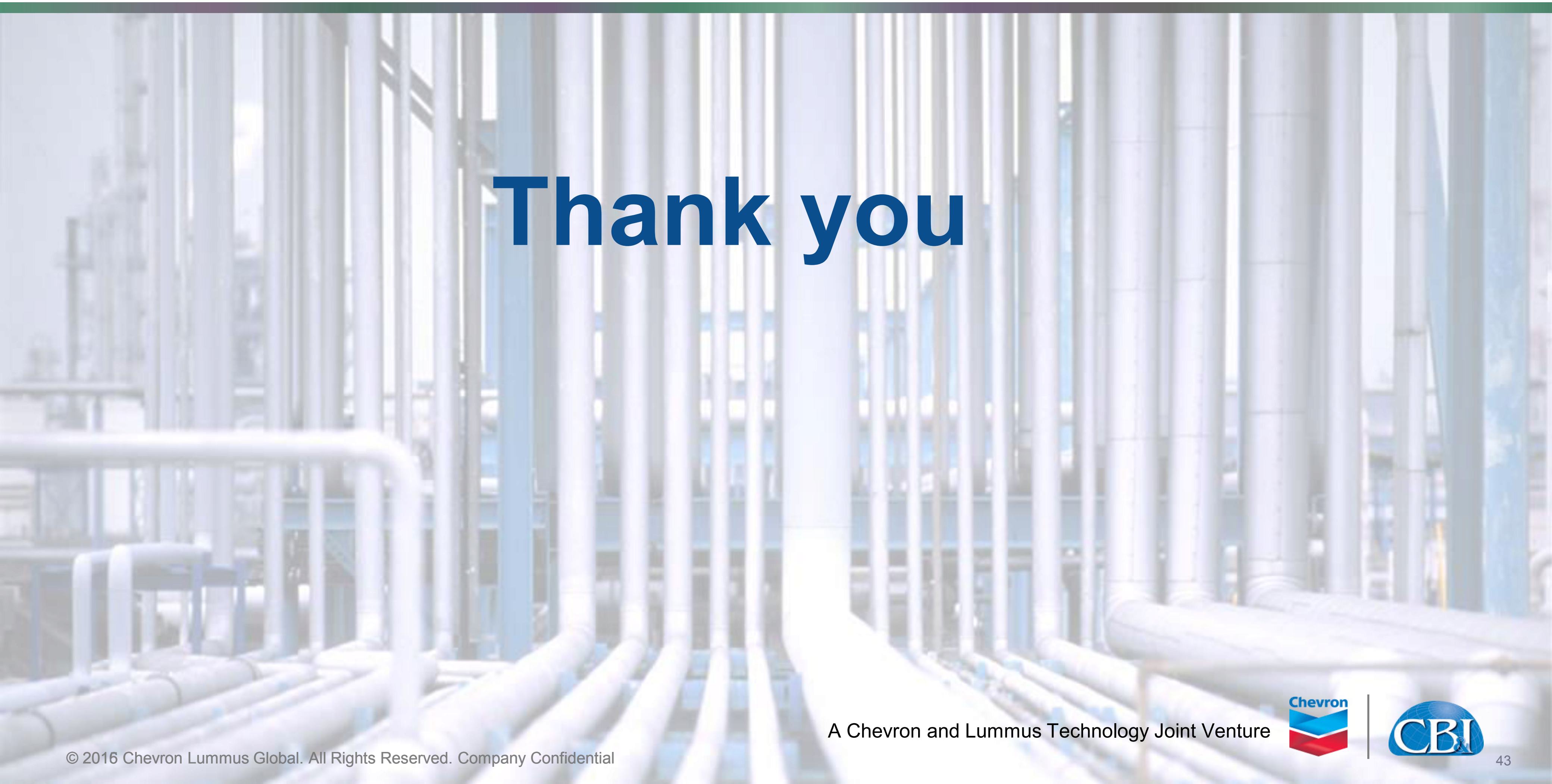

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